(12) PATENT ABRIDGMENT (11) Document No. AU-B-12783/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 601553

(54) Title
PROCESS FOR MAKING SUPERCONDUCTOR

International Patent Classification(s)
(51)[4] H01L 039/12 C01G 003/02 C01G 057/00 C04B 035/00
C04B 035/50 H01L 039/24

(21) Application No. : 12783/88 (22) Application Date : 08.03.88

(30) Priority Data

(31) Number (32) Date (33) Country
024653 11.03.87 US UNITED STATES OF AMERICA

(43) Publication Date : 15.09.88

(44) Publication Date of Accepted Application : 13.09.90

(71) Applicant(s)
INTERNATIONAL BUSINESS MACHINES CORPORATION

(72) Inventor(s)
ROBERT B. BEYERS; EDWARD M. ENGLER; PAUL M. GRANT; GRACE S. LIM; STUART S.P. PARKIN

(74) Attorney or Agent
SPRUSON & FERGUSON

(56) Prior Art Documents
AU 10699/88 C01G 3/02, 53/04, 37/02
AU 586940 10014/88 H01B 12/00,C01G 3/02, H01L 39/12,

(57) Claim

1. A process for making a single phase bulk electrical superconductor at a temperature above 77°K, said process comprising the steps of:

(1) intimately mixing in the form of powders, metal oxides or their precursors having a composition $A_{1\pm x}M_{2\pm x}Cu_3O_y$ wherein:

A is either Y or is two or more of Y, La, Lu, Sc or Yb;

M is either Ba or is two or more of Ba, Sr or Ca;

x is a value greater than or equal to 0 and less than or equal to 0.5; and

y is sufficient to satisfy the valence demands;

(2) heating the mixture to the temperature between about 800°C and about 1100°C in the presence of oxygen;

(3) slowly cooling the mixture to room temperature in the presence of oxygen over a period of at least four hours.

601553

S & F Ref: 50293

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

This document contains the amendments made under Section 49 and is correct for printing.

Priority:

Related Art:

Name and Address of Applicant: International Business Machines Corporation
Armonk
New York New York 10504
UNITED STATES OF AMERICA

Address for Service: Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Electrically Superconducting Compositions and Processes for their Preparation

The following statement is a full description of this invention, including the best method of performing it known to me/us

5845/3

In accordance with the present invention there is disclosed a process for making a single phase bulk electrical superconductor at a temperature above 77°K, said process comprising the steps of:

(1) intimately mixing in the form of powders, metal oxides or their precursors having a composition $A_{1\pm x}M_{2\pm x}Cu_3O_y$ wherein:

A is either Y or is two or more of Y, La, Lu, Sc or Yb;

M is either Ba or is two or more of Ba, Sr or Ca;

x is a value greater than or equal to 0 and less than or equal to 0.5; and

y is sufficient to satisfy the valence demands;

(2) heating the mixture to the temperature between about 800°C and about 1100°C in the presence of oxygen;

(3) slowly cooling the mixture to room temperature in the presence of oxygen over a period of at least four hours.

ELECTRICALLY SUPERCONDUCTING COMPOSITIONS AND PROCESSES FOR THEIR PREPARATION

Description

Technical Field

The present invention is concerned with electrically superconducting compositions which are useful at a temperature above 77°K and with methods for the preparation of such compositions.

Background Art

The technical breakthrough of Bednorz and Muller, Z. Phys. B, 64, 189 (1986), was the first major improvement in the superconducting transition temperature in the last decade. The material was of nominal composition $La_{2-x}M_xCuO_y$ where M=Ca, Ba or Sr, x was typically >0 and <0.3 and y was variable depending on preparation conditions. Superconductivity was found only over this narrow range of doping of M. The highest superconducting transition (Tc) was obtained for Sr doping and x equal to approximately 0.15-0.20 with Tc in the mid forty degree Kelvin range, Cava et al, Phys. Rev. Letters, 58, 408 (1987). Subsequently, it was reported in March 1987, Chu et al, Phys. Rev. Letters, 58, 405 (1987) that $Y_{1.2}Ba_{0.8}CuO_y$ displayed the onset of superconductivity in the mid ninety degree Kelvin range. In contrast to the earlier work on $La_{2-x}M_xCuO_y$, this higher temperature superconductor has been only prepared as a mixture of several unknown phases and only a minor fraction of the material actually goes superconducting. Experimentation by ourselves and other research groups have revealed that superconductivity is not a general phenomena in this class of materials. Even minor composition variations or isoelectronic atom substitutions will not show superconductivity. For example, Sr or Ca substitution for Ba in $Y_{1.2}Ba_{0.8}CuO_y$ did not produce superconductors.

Disclosure of the Invention

It has now been discovered that compositions having the formula $A_{1\pm x}M_{2\pm x}Cu_3O_y$ wherein x is typically between 0 and 0.5 and y is sufficient to satisfy the valence demands, are single phase bulk electrical superconductors at a temperature above that of liquid nitrogen, namely 77°K. The compositions have a perovskite-like crystalline structure. They are made by intimately mixing in the form of powders the metal oxides or precursors of metal oxides such as carbonates or hydroxides. The heating of the mixture is conducted at a temperature between about 800°C and about 1100°C in the presence of oxygen. The preferred temperature is about 900 to 1000°C. The heating is carried out for a period of time from about 10 to about 40 hours. In general, the lower the temperature, the longer the time required for heating. It is also a critical feature of the present invention that following the heating, the composition is slowly cooled to room temperature in the presence of oxygen over a period of at least four hours. Preferred compositions have formulas very close to $A_1M_2Cu_3O_y$ wherein A is Y, or a combination of Y, La, Lu, Sc or Yb and M is Ba, or a combination of Ba, Sr or Ca, and y is sufficient to satisfy the valence demands. The most preferred compositions are those in which A is Y and M is Ba. The most preferred composition exhibits single phase bulk electrical superconductivity at a temperature well above 77°K. It has a perovskite-like crystalline structure and consists essentially of a metal component having one atom of yttrium, two atoms of barium and three atoms of copper and a non-metal component of oxygen.

As an example of the most preferred method of preparing the most preferred composition, the following procedure is provided:

Oxides or carbonates of Y, Ba and Cu are thoroughly mixed, or alternately their soluble nitrate or chloride compounds are coprecipitated as their hydroxide or carbonate salts. The mixed powders are heated in an oven at 800-1100 degrees C in either oxygen or air for periods ranging from 10-40 hours. Oxygen gives better results. Longer heating times ensure

more homogeneous reaction of the starting compounds. Longer reaction times are required at the lower temperatures. To prepare rigid samples, the powders from the initial heating procedure are compressed into pellets or combined in polymeric binders and heated again under similar conditions. The use of an oxygen atmosphere when heating, and slow cooling of the oven to room temperature, are important for realizing the sharpest and highest superconducting transitions, and more bulk superconductivity. Typically, the oven is cooled from 900-1000 degrees C over about 5 hours to room temperature.

The compositions obtained by the above process have a perovskite-like structure which can have variable oxygen content depending upon the final annealing and cooling steps. Removal of oxygen, for example by heating in an inert or reducing atmosphere, suppresses superconductivity. Higher oxygen content leads to improved and higher superconducting properties. As mentioned above, it is essential that following the heating step, the compositions be cooled slowly. It is believed that this slow cooling is required because when the material is cooled slowly, it retains slightly more oxygen than when it is cooled rapidly.

The following materials have all demonstrated bulk superconductivity at a temperature above 77°K. They are all single phase perovskite-like crystalline structures within the general formula

$A_{1\pm x}M_{2\pm x}Cu_3O_y$

The materials are:

$(Y_{0.8}Lu_{0.2})_{1.0}Ba_{2.0}Cu_3O_y$

$(Y_{0.5}Lu_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$

$(Y_{0.5}La_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$

$(Y_{0.5}Sc_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$

$(La_{0.5}Sc_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$

$Y_{1.0}(Ba_{0.5}Ca_{0.5})_{2.0}Cu_3O_y$

$\cancel{Y_{1.0}(Sr_{0.5}Ca_{0.5})_{2.0}Cu_3O_y}$

$Y_{0.8}Ba_{2.0}Cu_3O_y$

$Y_{1.2}Ba_{2.0}Cu_3O_y$

$Y_{1.0}Ba_{1.8}Cu_3O_y$

$Y_{1.0}Ba_{1.5}Cu_3O_y$

$Y_{1.2}Ba_{1.8}Cu_3O_y$

All the above samples were confirmed to be superconductive by the AC magnetic susceptibility test method and by electrical resistivity measurements also.

To date, the following materials have not been found to be bulk single phase superconductors above 77°K when formulated and tested by the procedures described above:

$Lu_{1.0}Ba_{2.0}Cu_3O_y$

$Lu_{1.0}Ca_{2.0}Cu_3O_y$

$La_{1.0}Ba_{2.0}Cu_3O_y$

$La_{1.0}Ca_{2.0}Cu_3O_y$

$Sc_{1.0}Ba_{2.0}Cu_3O_y$

$Yb_{1.0}Ba_{2.0}Cu_3O_y$

$Y_{1.0}Ca_{2.0}Cu_3O_y$

$Y_{1.0}Ba_{1.0}Cu_{2.0}O_y$

$Y_{2.0}Ba_{1.0}Cu_{1.0}O_y$

Perhaps it is necessary that either yttrium be most of the A component, or that the combination of two or more related A components have an average atomic size approximately that of yttrium.

The range of compositions are not exactly defined as whole number atomic ratios of A and M because it seems that the crystalline structure can accommodate vacancies of these metals and still retain the necessary structure for the high temperature superconductivity. In these cases, as in all others, the oxygen is present in an amount to satisfy the valence demands.

There are a wide variety of current uses of superconductivity at

liquid helium temperatures which will be cheaper and more convenient to use at liquid nitrogen temperatures. The use of thin film and ceramic processing technologies will enable these materials to find applications in microelectronics, high field magnets, energy transmission, and electromechanical devices. In particular, these materials are useful in logic devices in computers (for example Josephson logic devices) and for interconnect metallurgy on and between chips as a means of improving speed and packaging density.

The claims defining the invention are as follows:

1. A process for making a single phase bulk electrical superconductor at a temperature above 77°K, said process comprising the steps of:

(1) intimately mixing in the form of powders, metal oxides or their precursors having a composition $A_{1\pm x}M_{2\pm x}Cu_3O_y$ wherein:

A is either Y or is two or more of Y, La, Lu, Sc or Yb;

M is either Ba or is two or more of Ba, Sr or Ca;

x is a value greater than or equal to 0 and less than or equal to 0.5; and

y is sufficient to satisfy the valence demands;

(2) heating the mixture to the temperature between about 800°C and about 1100°C in the presence of oxygen;

(3) slowly cooling the mixture to room temperature in the presence of oxygen over a period of at least four hours.

2. A process as claimed in claim 1 wherein the metal oxides or their precursors are yttrium oxide (Y_2O_3) or a precursor thereof, barium oxide (BaO) or a precursor thereof and cupric oxide (CuO) or a precursor thereof, in the mole ratio of 0.5 to 2 to 3.

3. A process as claimed in claim 1 or 2 wherein the temperature of the heating is between 900°C and 950°C.

4. A process as claimed in claim 1, 2 or 3 wherein the time of the heating is between 10 hours and 40 hours.

5. A process as claimed in any one of claims 1 to 4 wherein the cooling takes place over a period of from 5 to 10 hours.

6. A process for making a single phase bulk electrical superconductor at a temperature above 77°K substantially as described herein with reference to the examples.

DATED this TWENTY-SECOND day of JUNE 1990

International Business Machines Corporation

Patent Attorneys for the Applicant

SPRUSON & FERGUSON

IAD/1006o